TRANSITION METALS AS CATALYSTS
FOR PYROLYSIS AND GASIFICATION OF BIOMASS

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INTRODUCTION

We envision a two stage process for the conversion of lignocellulosic waste (such as sawdust or newsprint) into useful chemicals and simple gases. In the first stage, vacuum pyrolysis at relative low temperatures produces a charcoal, a condensible organic liquid (pyrolysis tar) and a noncondensible low Btu fuel gas. In the second stage, the charcoal which contains a major portion of the energy content of the feedstock is either pyrolyzed at high temperatures, or gasified to produce simple gases. The gasification is free from tar forming reactions, with the energy balance and product gas composition dependent on the composition of the reactant gas.[1,2]

The production of LG from vacuum pyrolysis of pure cellulose and wood has frequently been reported.(e.g.[3,4]) Higher yields of LG from wood pyrolysis were obtained by prior removal by acid washing of the indigenous metal ions bound to the hemicellulose in the wood. We have recently[5] studied the effect of individual metal ions (ion exchanged into wood) on gaseous products from pyrolysis of wood using coupled TG/FTIR. These studies showed that K but not Ca, acts as a catalyst in pyrolysis reactions resulting in formation of CO_2, CO, and formic acid (especially from polysaccharides), acetic acid (from hemicellulose), and methanol (from lignin). This type of study has now been extended to include a wider range of metal ions, and to embrace newsprint as well as wood. Since the major motivation in this work lies in the thermochemical utilization of lignocellulosic waste, we have especially included metal ions which are known to increase char yield and to act as catalysts in char gasification.

In this paper we are specifically concerned with air gasification of the chars doped with metal ions that result from LG producing pyrolyses (i.e. Fe and Cu-doped chars). Several studies have been made of the catalytic effects of copper and its salts in accelerating the oxidation of graphite.[6-9] In fact, copper is reported to be the most effective catalyst of the carbon-air reaction (for Spanish lignite char) of the first transition series of elements.[10,11] The same authors report (for air gasification of Cu-doped lignite char) a dramatic jump from a region of low reactivity and high apparent activation energy to a region of high reactivity and low apparent activation energy for a 5°C temperature increase.[12]

This laboratory has also observed this jump phenomenon for copper catalysis[13] and for iron catalysis[14] in the air gasification of cellulosic chars.   For this study we utilized carboxymethylcellulose (CMC) for incorporation of ion exchanged cations and cellulose fibers (CF-11) for incorporation of salts by sorption from aqueous solution. The doped cellulosic fibers were then pyrolyzed to chars for gasification studies. We were able to report "jump temperatures" (T_j, defined by Moreno-Castilla et al.[12] as the lowest temperature of the high reactivity region) for ion-exchanged Cu CMC and sorbed Cu salt CF-11 samples.

Part of this paper reports our continued study of this jump phenomenon. We use the approach described above (*viz.* copper doped CMC and CF-11 samples) since we are able to achieve particularly exact control of the distribution of the metal species in the cellulosic substrates and hence in the char.

EXPERIMENTAL

The ion-exchanged wood (milled cottonwood sapwood, *Populus trichocarpa*) and carboxymethylcellulose (CMC) and salt-sorbed samples were prepared as described earlier.[15, 16] Newsprint samples were prepared from the Wall Street Journal, macerated with deionized water (or salt solutions for salt-sorbed newsprint) in a Waring blender, filtered and air-dried to a mat ca. 2 mm thick. The mats were cut into cubic pellets (ca. 2 mm^3) before pyrolysis. Metal ion contents were measured by inductively coupled argon plasma spectrometry (see *Tables 1* to *4*).

Pyrolyses were carried out at 2 Torr under flowing nitrogen as described previously[17] with tars condensed at room temperature and "distillate" condensed at -50°C. LG contents of tars were determined by GLC of tri-O-methylsilyl ethers[17] and the compounds in the second condensate (other than water) were determined by ^{1}H NMR.[18] The yield of levoglucosenone (LGO) in the second distillate was determined by relating the integrated signal for the C-1 hydrogen (5.31 ppm, s, 1H)[19] to the internal standard (2-methyl-2-propanol; 1.21 ppm, s, 9H).

The thermogravimetry system used to measure gasification rates has been described.[13] The samples were first pyrolyzed at a heat treatment temperature (HTT) for 15 min in nitrogen *in situ* (80 mL min^{-1}), and subsequently gasified (gasification temperature = GT) in air (80 mL min^{-1}, 22% O_2). The TG balance was purged with helium (20 mL min^{-1}). The temperature program and weight loss curve of a typical gasification experiment are shown in *Figure 1*.

The apparatus for measuring differences in sample and furnace temperatures is described elsewhere.[20] Essentially, a thermocouple was placed in the furnace near to the sample (similar to TG temperature measurement) and a second thermocouple embedded in the sample. The temperature program and gas flow control was similar to a typical gasification, and during the course of the experiment the two thermocouple readings were compared.

RESULTS AND DISCUSSION

Pyrolysis of Ion-exchanged Wood

The yields of char, tar, and distillate from the pyrolysis of ion-exchanged wood are shown in *Table 1*. The alkali metal and calcium wood samples showed increased char formation, low tar and high distillate yield compared to acid-washed wood. All other ion-exchanged wood samples showed char and tar yields similar to acid-washed wood, with the transition metals especially favoring tar formation. The analysis of the tar for LG shown in *Table 1* indicates that the tars from Li, K and Ca wood samples were not only obtained in reduced yield, but also contained a lower proportion of LG than tar from acid-washed wood. All other metal ions produced yields of LG above 10.5% compared with 5.4% from acid-washed wood. In other words, wood samples ion-exchanged with transition metals gave higher yields of a cleaner tar.

The best yield of LG observed was 15.8% from the ferrous wood sample. Assuming that LG is derived only from cellulose and that the latter represents 50% of the wood,[21] then the conversion of cellulose to LG was 31.6%. This yield may be compared with 41.5% obtained from pure cellulose (CF-11 cellulose).

The mechanism whereby the yield of LG is increased by the presence of these metal ions is not known. However, since cupric acetate sorbed in pure cellulose does not catalyze the formation of LG, we tentatively conclude that catalysis of LG formation in wood may involve some interaction with lignin. The low yield of LG from original wood (0.4%) is probably associated with two inhibiting factors, *viz.* indigenous metal ions (especially K and Ca) and lignin. When the metal ions are removed by acid washing, the LG yield increases to 5.4% (*i.e.* 10.8% based on cellulose), but the lignin effect presumably holds the LG yield well below that from cellulose (41.5%). The presence of some metal ions, especially the transition metals, may decrease the interference by lignin in the conversion of cellulose to LG.

Pyrolysis of Wood Sorbed with Salts
Since the improved yields of LG from wood pyrolysis induced by the presence of added metal ions are of considerable interest (in connection with thermochemical utilization of biomass), this study was extended to determine whether it is necessary to remove the indigenous cations in the wood, and whether the "beneficial" metal ion can be added more simply and economically as salts by sorption rather than by ion-exchange. This study concentrated on cuprous and ferrous salts because these ions were most effective in increasing LG and charcoal yields when ion-exchanged, and also because the chars from such pyrolyses are likely to contain elemental Cu or active Fe species which are known to be catalysts of gasification reactions.[13]

The products of pyrolysis of wood sorbed with cupric acetate, ferrous acetate and ferrous sulfate are shown in *Table 2*. The addition of cupric ion by sorption of the acetate salt in acid-washed wood (to 0.45% Cu) is effective in increasing LG yield to 11.2%; higher concentrations of copper did not significantly improve the LG yield. When the indigenous ions (predominantly K and Ca) are not removed by acid washing before addition of the cupric acetate, the improvement in LG yield is much less marked. The indigenous cations negate some of the catalytic influence of the Cu. The results with sorbed ferrous acetate were similar, although the LG yield with the salt sorbed in the acid-washed wood (7.5%) was considerably less than for the corresponding ion-exchanged wood (15.8%).

The pyrolysis of wood sorbed with ferrous sulfate was studied as an example of an anion likely to remain in the pyrolyzing solid and to generate acid conditions (acetate ions are lost from the solid at the pyrolysis temperature). Acid-washed wood containing ferrous sulfate yielded 6.1% LG and an additional 3.0% levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranos-2-ulose, LGO), which was found in the distillate. LGO is a known product of acid-catalyzed cellulose pyrolysis[22] and its formation was observed only in the presence of the sulfate anion.

Application to Newsprint
Newsprint comprises about one-third of the solid municipal waste in developed countries, it is likely soon to be excluded from landfill disposal and there is a limit to the proportion which can be recycled into paper. Thermochemical processes have the potential to account for the utilization of large amounts of waste newsprint. Our sample contained 24% lignin.[23] It was therefore expected, on the basis of the above experiments with wood, to be similarly amenable to the "beneficial" effects of ferrous sulfate in terms of increased LG and LGO yields.

Table 3 shows the influence of sorbed ferrous sulfate on products of pyrolysis in nitrogen at 400°C for 30 min. In the absence of added ferrous sulfate, pyrolysis of newsprint yielded 3.2% LG, but no LGO. Sorption of ferrous sulfate (to 2.08% $FeSO_4$) before pyrolysis increased the yield of LG to 16.6%, and also yielded 4.2% LGO. Char yield also increased from 15% for newsprint to 20% for $FeSO_4$ sorbed newsprint. Thus we have a procedure to generate chemical

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feedstocks (LG and LGO) from pyrolysis of newsprint, while simultaneously forming in increased yield a char which already contains an efficient gasification catalyst.

Gasification of Cu and Fe ion-exchanged CMC chars

We have previously reported the effect of HTT and mode of addition of metal ions on the Tj of Cu-doped chars.[16] Jump temperatures were determined in a series of gasification experiments where GT was successively lowered 5°C until the low reactivity region was reached. The Tj for Fe-doped CMC char (HTT 400°C, [Fe] 2.47% d.a.f.), determined by the same method, was 295°C. *Figures 2* and *3* show rate-time plots for the gasification in air of Cu- and Fe-doped cellulose chars (HTT 400°C) at and below the jump temperature (Tj = 255°C for Cu and 295°C for Fe). Copper appears to be a superior catalyst over iron; the Tj of Cu is lower and the rate maximum (Rg(max)) is higher. In the case of Cu-doped chars, the initial rate of gasification increases *ca.* 160-fold for a 5°C temperature increase at Tj.

In a series of experiments to determine the effect of Cu concentration on Tj we gasified Cu-doped CMC chars in a temperature program (HTT 400°C, GT 200°C + 5°/min). *Table 4* shows the effect of Cu concentration on the apparent Tj. Increasing Cu concentration in the range shown in *Table 4* effected a decrease in the apparent Tj but did not change Rg(max). We expected to measure Tj as the temperature at which the rate suddenly increased, and that the Tj of our CuCMC-1 sample would be as previously determined (*i.e.* 255°C). However, the Tj of CuCMC-1 determined by this method was significantly different. We conclude that this jump in reactivity is also affected by the thermal history of the char.

Effect of oxygen chemisorption on sample temperature in the furnace

It seemed likely, based on the observation of small spikes in the TG thermocouple reading on the introduction of air into the furnace (see *Figure 1*), that the TG apparatus may not be recording the true temperature of the sample during rapid gasification. In fact, when a *ca.* 20 mg CuCMC-1 char (HTT 400°C) was gasified (GT 260°C) with a thermocouple in contact with the char, the temperature of the char ran ahead of the furnace temperature soon after air was admitted (see *Figure 4*).

We have reported[20] that for calcium-doped chars prepared at relatively low temperatures (*e.g.* HTT 400°C), the initial rate of gasification in air (Rg(max) from TG) is extremely high for a short time. This effect was shown to be due to "run away" temperature increase associated with exothermic oxygen chemisorption. In this case the effect can be avoided by pre-sorption of oxygen below the gasification temperature. However, unlike calcium-doped chars, in the copper-catalyzed gasification the initial high Rg(max) peak at GT 260°C could not be eliminated by pre-sorption of oxygen at 200°C (see *Figure 5*). We conclude that exothermic oxygen chemisorption contributes to, but does not fully account for the jump phenomenon in copper catalysis of gasification.

It seems likely that this jump in reactivity is associated with the mobility of the metal species acquired at the Tammann temperature,[12] and that jumps in reactivity below the Tammann temperature can be explained by the thermal history of the sample and its heat capacity, and by the heat generated by oxygen chemisorption.

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Table 1. Vacuum pyrolysis of ion-exchanged wood

Sample	Metal ion (% d.a.f.)[a]	char (% d.a.f.)	Tar (% d.a.f.)	Distillate (% d.a.f.)	LG (% d.a.f.)
Acid-Washed Wood	----[b]	19	43	16	5.4
Li	----	19	25	44	0.7
Mg	0.08	16	45	29	10.5
K	0.20	22	21	40	0.4
Ca	0.14	20	32	27	4.1
Mn[II]	0.19	15	44	29	10.6
Fe[II]	0.37	15	50	30	15.8
Co[II]	0.20	15	49	29	12.4
Ni[II]	----	14	56	25	13.0
Cu[II]	0.19	17	54	26	13.5
Zn	0.26	16	45	31	11.4
CF-11 cellulose	----	13	67	14	41.5
CuAc$_2$/CF-11[c]	----	24	51	14	31.0

a % weight based on dry ash free wood. Pyrolysis at 350°C/30 min.
b Not determined
c Cupric acetate sorbed on CF-11 (not ion-exchanged)

Table 2. Vacuum pyrolysis of wood sorbed with salt solution

Sample	Metal ion (% d.a.f.)[a]	char (% d.a.f.)	Tar (% d.a.f.)	Distillate (% d.a.f.)	LG (% d.a.f.)
Original wood		15	25	24	0.4
Acid-Washed (AW)		19	43	16	5.4
AW/CuAc$_2$	0.45	29	38	----[b]	11.2
AW/CuAc$_2$	0.74	30	40	---	11.2
AW/CuAc$_2$	1.10	20	42	---	12.5
CuAc$_2$	0.43	15	43	21	5.9
AW/FeAc$_2$	3.34	22	24	26	7.5
FeAc$_2$	3.18	28	19	28	5.2
AW/FeSO$_4$[c]	1.43	38	18	25	6.1

a % weight based on dry ash free wood. Pyrolysis at 350°C/30 min.
b Not determined
c Pyrolysis at 300°C/60 min

Table 3. Vacuum pyrolysis products from newsprint (NP)[a]

Sample	char	Tar	Distillate	LG	LGO
Original NP	15	44	32	3.3	ND
NP + 2.08% FeSO$_4$	20	43	37	16.6	4.2

a % weight based on dry ash free wood. Pyrolysis at 400°C/30 min.
ND not detected

Table 4. The Effect of Copper Concentration on the Apparent Jump Temperature[a]

Sample	Cu in char (% d.a.f.)	Tj (°C)	Rg(max) (min^{-1})
CuCMC-1	2.82	312	1.6
CuCMC-2	1.54	320	1.8
CuCMC-3	0.67	340	1.8

a For HTT 400°C, GT 200°C + 5°/min

Figure 1.   CuCMC-1 Gasification in air
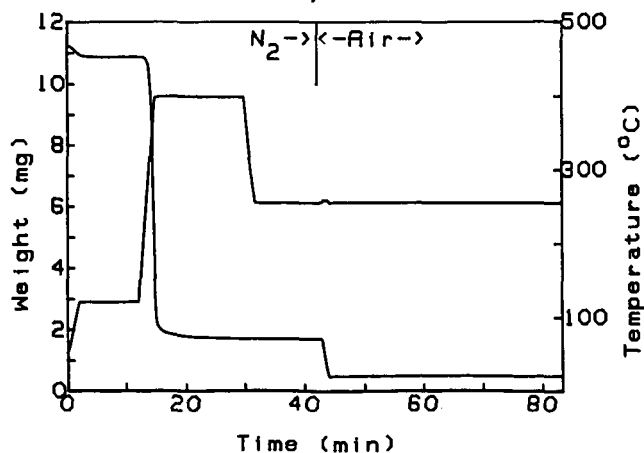HTT 400°C, GT 255°C
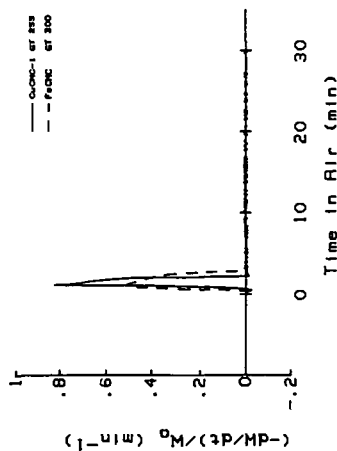
Figure 2. DTG Curves for Fe and Cu CMC at T_J

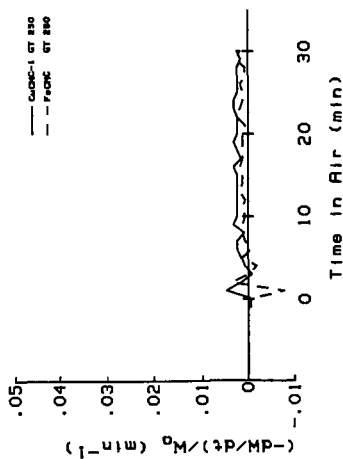Figure 3. DTG Curves for Fe and Cu CMC Below T_J
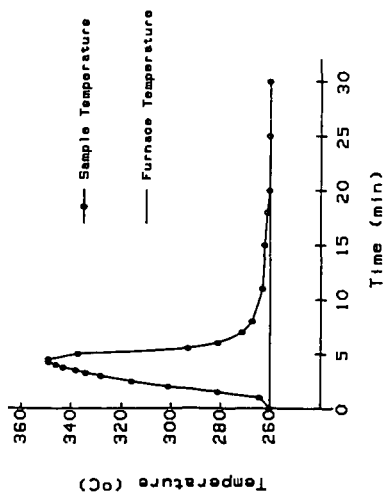
Figure 4. CuCMC-1 Gasification in Air (HTT 400)

Figure 5. CuCMC-1 Gasification with Pre-sorption at 200°C